

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/232002784>

# Atomic Layer Deposition of Aluminum Nitride Thin films from Trimethyl Aluminum (TMA) and Ammonia

Article in MRS Online Proceeding Library Archive · January 2004

DOI: 10.1557/PROC-811-D1.9

---

CITATIONS

19

READS

1,044

4 authors, including:



Xinye Liu

Western Digital Corporation

24 PUBLICATIONS 298 CITATIONS

SEE PROFILE

## Atomic Layer Deposition of Aluminum Nitride Thin films from Trimethyl Aluminum (TMA) and Ammonia

Xinye Liu, Sasangan Ramanathan, Eddie Lee, and Thomas E. Seidel  
Genus, Inc., 1139 Karlstad Drive, Sunnyvale, CA 94089

### ABSTRACT

Aluminum nitride (AlN) thin films were deposited from trimethyl aluminum (TMA) and Ammonia (NH<sub>3</sub>) by thermal atomic layer deposition (thermal ALD) and plasma enhanced atomic layer deposition (PEALD) on 200 mm silicon wafers. For both thermal ALD and PEALD, the deposition rate increased significantly with the deposition temperature. The deposition rate did not fully saturate even with 10 seconds of NH<sub>3</sub> pulse time. Plasma significantly increased the deposition rate of AlN films. A large number of incubation cycles were needed to deposit AlN films on Si wafers. 100% step coverage was achieved on trenches with aspect ratio of 35:1 at 100 nm feature size by thermal ALD. X-ray diffraction (XRD) data showed that the AlN films deposited from 370 °C to 470 °C were polycrystalline. Glancing angle X-ray reflection (XRR) results showed that the RMS roughness of the films increased as the film thickness increased.

### INTRODUCTION

Because of its outstanding properties such as excellent thermal and chemical stability, high thermal conductivity, low thermal expansion coefficient, and wide band gap, AlN has been well studied for various applications such as IC packaging<sup>[1]</sup>, optoelectronic devices<sup>[2]</sup> and diffusion barriers<sup>[3]</sup>. A number of methods have been used to deposit AlN<sup>[3,4,5,6]</sup>. Due to its high dielectric constant (~ 8), we are interested in AlN's applications in depositing high dielectric constant materials such as aluminum oxynitride (AlON) and aluminum silicon oxynitride (AlSiON) for the next generation microelectronic devices by ALD. To deposit AlON or AlSiON with desired properties, it is essential to understand deposition of AlN. In this study, we investigated ALD of AlN from TMA and NH<sub>3</sub>, especially the deposition rate, microstructures, and the differences between thermal ALD and PEALD.

### EXPERIMENTAL

The ALD reactor used in this work was a Genus StrataGem™ ALD system. TMA and NH<sub>3</sub> vapor was delivered into the reactor chamber vertically with a Genus precursor delivery system. The vapor was then distributed by a gas distributor which was also the bottom electrode for plasma generation. The TMA concentration in the reactor was 10% to 15% in partial pressure. The NH<sub>3</sub> concentration in the reactor was 20% to 30% in partial pressure. The stainless steel gas lines for delivering the precursors were heated up to 160 °C. Nitrogen was used as the TMA carrier gas and purge gas. No carrier gas was used for NH<sub>3</sub>. The process chamber pressure was from 100 mTorr to 500 mTorr. The set point of susceptor (the Si substrate holder) temperature was from 200 °C to 470 °C. The actual substrate temperature was 25 °C to 30 °C lower than the

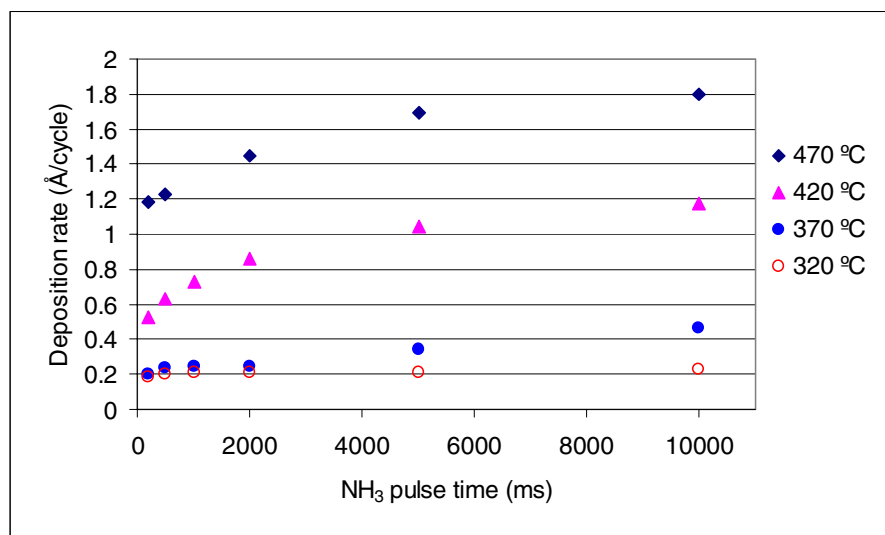
set point. The substrates were 200 mm planar Si (100) wafers for most of characterizations. The wafers were etched by HF vapor prior to the deposition. The RF plasma frequency was 13.56MHz. The plasma power was 50 W to 300 W. The plasma was turned on only during NH<sub>3</sub> pulse time. For step coverage measurements, patterned wafers with elliptical holes of 0.17  $\mu\text{m}$  by 0.22  $\mu\text{m}$  by 7.5  $\mu\text{m}$  deep etched in silicon were used. The reactor was a warm wall reactor with a wall temperature of 120 ~ 160  $^{\circ}\text{C}$ . Trimethyl aluminum (TMA) of 99.99% chemical purity purchased from Epichem Chemicals was used as aluminum precursor. The TMA container was at room temperature, corresponding to a vapor pressure of 10 Torr<sup>[7]</sup>.

The film thickness was measured with a spectroscopic Ellipsometer made by the J. A. Woollam Co., Inc., using 16 points along the radius from 0 mm to 97 mm from the center of the wafer. The thickness uniformity and the temperature dependence of the deposition rate were calculated based on the thickness measurements. Step coverage was measured by scanning electronic microscopy (SEM).

## RESULTS

### Deposition Rate of Thermal ALD

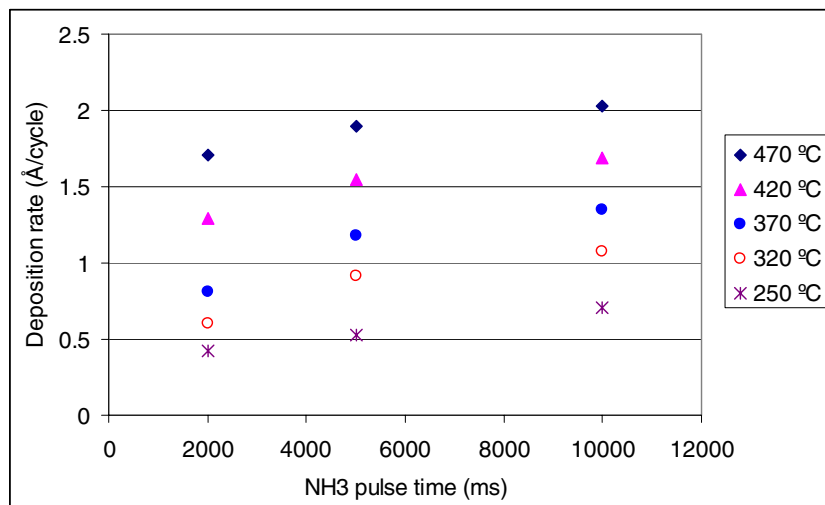
The deposition rate of the thermal ALD processes was characterized at different temperatures with different NH<sub>3</sub> pulse time (Figure 1). The deposition rate was very low at 320  $^{\circ}\text{C}$ . As the susceptor temperature increased, the deposition rate increased significantly. The data can be fitted into an Arrhenius equation with an activation energy of 0.53, 0.56, and 0.55 eV for NH<sub>3</sub> pulse time of 2, 5, and 10 seconds, respectively. The deposition rate did not saturate even with 10 seconds of NH<sub>3</sub> pulse time, suggesting a non self-limiting half-reaction.



**Figure 1.** The deposition rate of thermal ALD processes at different susceptor temperatures with different NH<sub>3</sub> pulse time. The deposition rate increased with the temperatures significantly.

## Deposition Rate of PEALD

The deposition rate of PEALD was characterized at different temperatures with different  $\text{NH}_3$  pulse time (Figure 2). It showed a similar trend as thermal ALD except that the deposition rate of PEALD is much higher than that of thermal ALD. Even at 250 °C, the deposition rate of PEALD is still potentially useful. The data can be fitted into an Arrhenius equation with an activation energy of 0.16, 0.19, and 0.21 eV for  $\text{NH}_3$  pulse time of 2, 5, and 10 seconds, respectively. The lower activation energy of PEALD is consistent with the observation that PEALD has a higher deposition rate than thermal ALD.



**Figure 2.** The deposition rate of the PEALD processes at different temperatures with different  $\text{NH}_3$  pulse time. The plasma power was 50 Watts.

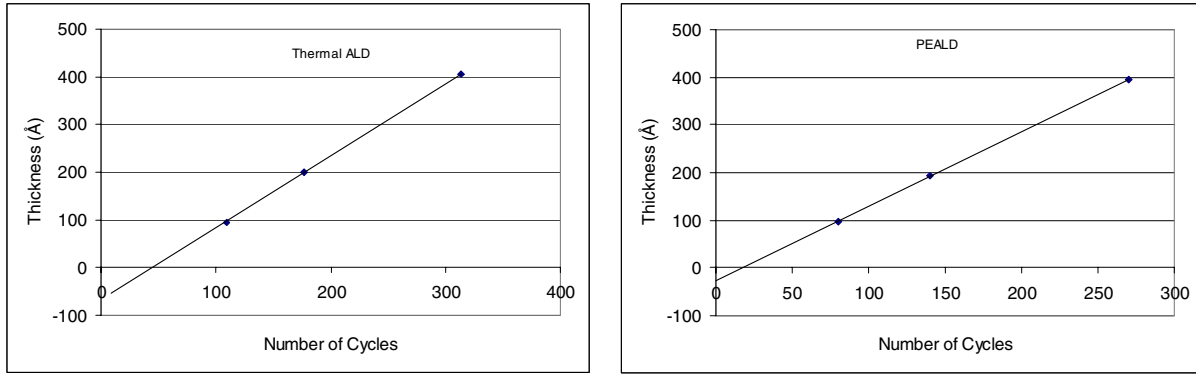
Again, the deposition rate did not saturate even with 10 seconds of  $\text{NH}_3$  pulse time. The deposition rate of PEALD increased with the plasma power. However, it also increased the within wafer non-uniformity (WIWNU) of the films (Table 1). This may be caused by the poorer ion concentration distribution of at the higher plasma power.

**Table 1.** Plasma power dependence of the deposition rate and the WIWNU.

Power (W)	50	100	200
Dep rate (Å/cycle)	0.90	1.27	1.73
WIWNU (%)	1.12	4.36	8.31

## Linearity

It was found that the thickness of both the thermal ALD and the PEALD  $\text{AlN}$  films increased linearly with the number of ALD reaction cycles (Figure 3a & 3b) if the number of cycles were large enough (>80). The x-intercept of the data fitting line is 41 for thermal ALD and 17 for PEALD. The positive x-intercept suggests that a large number of incubation cycles were needed before the deposition went into the "linear growth" regime. This is different from ALD of  $\text{H}_2\text{O}$  based  $\text{Al}_2\text{O}_3$  or  $\text{HfO}_2$ , both have only a few incubation cycles<sup>[8]</sup>.



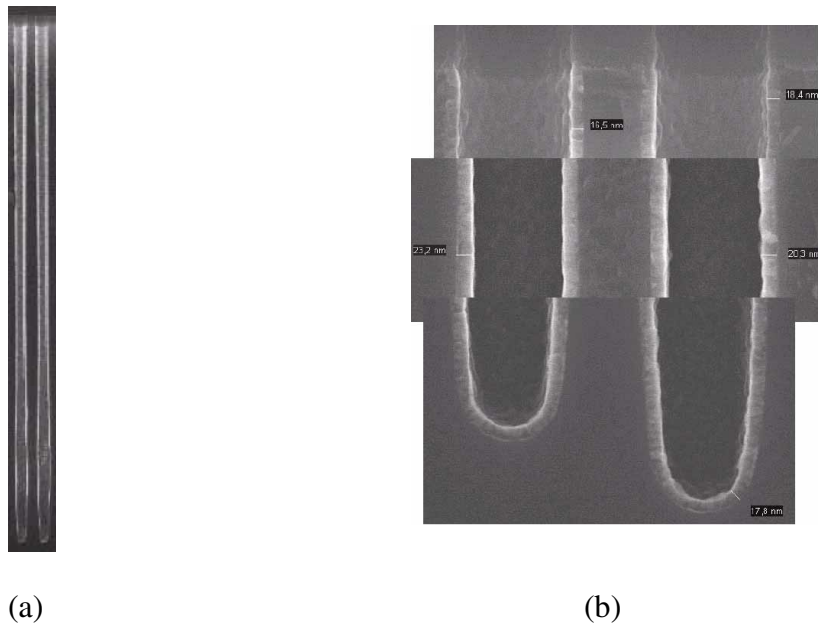
(a)

(b)

**Figure 3.** The AlN film thickness increased linearly with the number of ALD reaction cycles in both (a) thermal ALD and (b) PEALD.

### Step Coverage

Approximately 100% step coverage was achieved by thermal ALD on patterned 200 mm wafer with deep trenches that has high aspect ratio of 35:1 (Figure 4a and 4b). The SEM images also showed that the film was quite rough.



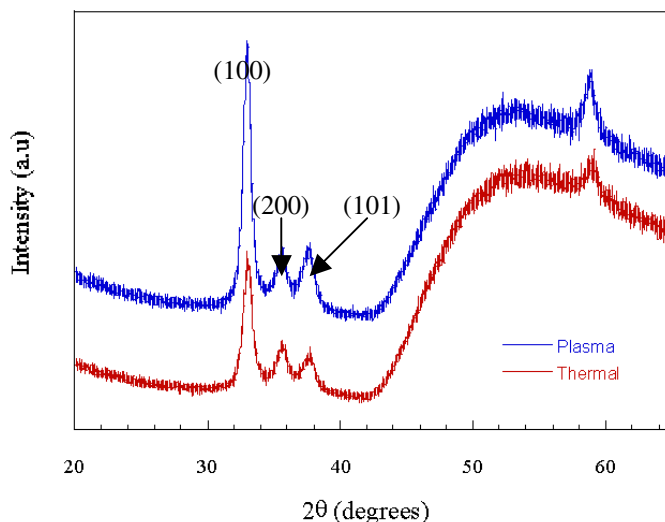
(a)

(b)

**Figure 4.** (a) Trenches with aspect ratio of 35:1. (b) Step coverage of the AlN film deposited by thermal ALD is nearly 100%.

### Crystallinity

Both the thermal ALD and the PEALD samples for x-ray diffraction measurement were prepared at 420 °C. The thickness of the thermal ALD and the PEALD samples was 820 Å and 800 Å, respectively.



**Figure 5.** X-ray diffraction data of thermal ALD (lower) and PEALD (upper) AlN films.

The (100) peak of the PEALD sample is sharper than that of the thermal ALD sample, and the ratio of the intensity of the (100) peak to the background of the PEALD sample is higher than that of the thermal ALD sample, both suggesting a higher degree of crystallization of the PEALD sample. The ratio of the intensity of the (100), (002), and (101) peaks of polycrystalline AlN is 100:60:80. For the PEALD sample, the ratio is 100:18:20. For the thermal ALD sample, the ratio is 100:31:25. The relative intensity of the (100) peak is higher than that of the other 2 peaks, suggesting a preferred (100) orientation for both the thermal ALD films and the PEALD films.

### **Roughness**

The roughness of the thermal ALD films and the PEALD films with different thickness was derived from the glancing angle x-ray reflection data. The roughness increased as the film thickness increased. The PEALD films had slightly higher roughness.

Table 2. Roughness of thermal ALD and PEALD AlN films

Thickness (Å)	Thermal ALD (Å)	PEALD (Å)
100	6	8
200	8	10.5
400	11	13

## **DISCUSSION**

Neither thermal ALD nor PEALD processes showed a good self-limiting behavior in this study. This may be due to  $\text{NH}_3$  adsorption. Since  $\text{NH}_3$  molecules adsorb on the surface very

strongly, the time needed to remove all the physically adsorbed  $\text{NH}_3$  molecules may be much longer than the ALD cycle time. The extra  $\text{NH}_3$  can react with more TMA, which means more TMA is needed to saturate the surface. Our preliminary data did show that TMA half reaction did not saturate with even 4 seconds of TMA pulse time. The temperature dependence of the deposition rate also showed that the reaction was not in the mass (flow) limiting range. An FTIR study of  $\text{NH}_3$  adsorption/desorption at various surface temperatures should give some insight in this matter.

The step coverage data showed that even without perfect saturation the step coverage was still very good. The reason may be that the reaction in our study was still a surface reaction.

## CONCLUSIONS

Crystalline AlN thin films were deposited from TMA and  $\text{NH}_3$  by both thermal ALD and PEALD. PEALD has much higher deposition rate and can deposit AlN films at much lowered substrate temperatures. The deposition rate of PEALD increased as the plasma power increased. A large number of incubation cycles was observed in both thermal ALD and PEALD processes. The PEALD processes needed much fewer incubation cycles than the thermal ALD processes, though the number of incubation cycles was still very large compare to  $\text{H}_2\text{O}$  based  $\text{Al}_2\text{O}_3$  and  $\text{HfO}_2$  ALD processes. 100% step coverage was achieved by thermal ALD at 420 °C. X-ray diffraction showed that both thermal ALD and PEALD films were crystalline with a preferred (100) orientation. However, PEALD films showed a higher degree of crystallization.

## ACKNOWLEDGEMENT

We thank Dr. Francois Fabreguette and Professor Steven George for the x-ray diffraction and reflection measurements.

## REFERENCES

- <sup>1</sup> J. W. Lee, J. J. Cuomo, B. F. Moody, Y. S. Cho, and R. L. Keusseyan, *Mat. Res. Soc. Symp. Proc.* Vol 783, B5.10.1, (2003)
- <sup>2</sup> A. T. Sowers, J. A. Christman, M. D. Bremser, B. L. Ward, R. F. Davis, and R. J. Nemanich, *Appl. Phys. Lett.* Vol. 71, 2289 (1998)
- <sup>3</sup> Roy G. Gordon, David Hoffman, and Umar Riaz, *J. Mater. Res.*, Vol. 6, No. 1, 5 (1991)
- <sup>4</sup> B. Luo, F. Ren, M. A. Mastro, D. Tsvetkov, A. Pechnikov, V. Soukhoveev, V. Dmitriev, K. H. Baik, and S. J. Pearton, *Mat. Res. Soc. Symp. Proc.* Vol. 764, C2.3.1 (2003)
- <sup>5</sup> R. M. Guerrero and J. R. V. Garcia, *Superficies y, Vacio* 9, 82, Diciembre 1999
- <sup>6</sup> Diana Riihelä, Mikko Ritala, Raija Matero, Markku Leskelä, Janne Jokinen and Pekka Haussalo, *Chemical Vapor Deposition*, Vol. 2, 277 (1996)
- <sup>7</sup> MSDS of TMA from Epichem, available at <http://www.epichem.com>
- <sup>8</sup> M. L. Green, M.-Y. Ho, B. Busch, G. D. Wilk, T. Sorsch, T. Conard, B. Brijs, W. Vandervorst, P. I. Räisänen, D. Muller, M. Bude, and J. Grazul, *J. Appl. Phys.* Vol. 92, 7168 (2002)